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Two test methods for mercury are described along with the laboratory and field studies done in developing and validating them. One method describes how to homogenize and analyze large quantities of sewage sludge. The other test method describes how to measure the mercury emissions from the stacks of sewage sludge incinerators. In this latter method, the samples are collected in a potassium permanganate/sulfuric acid solution and analyzed for mercury using flameless atomic absorption.

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TEST METHODS TO DETERMINE THE MERCURY EMISSIONS FROM SLUDGE INCINERATION PLANTS

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Toxic Substances and the Office of Enforcement.

This study was conducted to develop improved test methodology for measuring the mercury emissions from sludge treatment plants. Two methods were developed and evaluated. One method deals with measuring the mercury content of the stack gases while the other deals with measuring the mercury content of the sludge.

PREFACE

U.S. Environmental Protection Agency (EPA) regulations limit the total atmospheric emissions of mercury from sewage sludge drying and incineration plants to 3200 grams per 24-hour day (1).

These emissions can be measured either directly by means of a stack test or, as is usually done, indirectly by means of a sludge analysis [EPA Method 105] (1). If sludge analysis is selected, three sludge samples are collected over a 24-hour period such that each sample represents a composite of eight consecutive 200- to 400-ml grab samples collected at one-hour intervals. The total weight of sludge processed in that 24-hour interval is then multiplied by the average concentration of mercury found in the samples to obtain an estimate of the daily mercury emission from the plant.

The sludge analysis procedure assumes that all the mercury in the sludge enters the atmosphere, which is unlikely. Thus, if a sludge incinerator potentially exceeds the emission standard based on this sludge analysis, a stack test is generally conducted using EPA Reference Method 101 (1,2); a test method in which the mercury emissions are collected in acidic iodine monochloride (ICl) and analyzed by cold vapor (flameless) atomic absorption spectrometry (FAA).

After promulgation of the mercury standard, an unpublished study by EPA indicated that both methods were inadequate for characterizing the mercury emissions from these plants. The studies described below were done to find suitable methods for determining the mercury content of sewage sludge and the mercury emissions from sewage sludge incinerators. For simplicity, the procedure for sludge analysis is described separately from the procedure for measuring the stack emissions. The actual test methods are described in Appendix A (Stack Test Method) and Appendix B (Sludge Test Method).

ABSTRACT

Two test methods for mercury are described along with the laboratory and field studies done for their development and validation.

One method describes how to effectively homogenize large volumes of sewage sludge using a mortar-mixer prior to mercury analysis. It was discovered that manual mixing of sludge was inadequate for ensuring an even distribution of mercury throughout the bulk sample prior to analysis. Furthermore, mercury content of sludge varied in a non-predictable manner with time. The second method described an improved procedure for measuring the mercury emissions from stacks on sewage sludge incinerators. Stack samples were collected in a solution of 4 percent potassium permangate in 10 percent sulfuric acid and analyzed for mercury using flameless atomic absorption spectrometry.

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SECTION 1

STACK SAMPLING METHOD

INTRODUCTION

Method 101 was originally promulgated as the Reference Method for measuring mercury emissions from mercury cell chlor-alkali plants (2). These plants differ significantly from sludge incineration plants in the following ways: 1) chlor-alkali plant stack emissions are essentially elemental mercury and often range from 1000 to 30,000 μg Hg/m^3, whereas the sludge incineration plant stack emissions may contain mercury in compound form and can range from 50- to 300-μg Hg/m^3; and 2) chlor-alkali stackgas is quite clean (containing a mixture of air, chlorine, and elemental mercury). In contrast, the incineration plant stack gas can contain sooty particulate, 15 to 30% water, mercury, other metals and significant amounts of oxidizable organic material.

When Method 101 was subjected to a collaborative test in 1974 using samples collected from a mercury cell chlor-alkali plant, it yielded imprecise and inaccurate results (3). Based on these results, the method was later revised to simplify the analytical procedure and to improve the mercury aeration system (4). A collaborative test showed that the revised method was highly precise and quite accurate (4).

One restriction in the revised procedure limited the ICl concentration in the aeration system to 0.0001M. At higher ICl concentrations, potassium iodide (KI), which is used to prepare the ICl reagent, inhibits the reduction of mercury by tin(II)chloride (4,5). This restriction, coupled with the low mercury levels present in the stack gas, caused the revised Method 101 to be unsuitable for sludge incinerator stack samples (6).

The study described below was done to find a suitable method for determining mercury emissions from sludge incinerator plant stacks. Two methods were investigated in-depth. One method employed ICl as the collecting liquid and mercury analysis by neutron activation analysis (NAA). The other method used $KMnO_4$ as the collecting liquid and mercury analysis by flameless atomic absorption (FAA). To check for method bias some $KMnO_4$ samples were also analyzed by NAA.

CONCLUSIONS AND RECOMMENDATIONS

Sampling results from sludge incinerators show that the final mercury concentration in a sampling train operated at 20 ℓ/min for two hours will range from 0.2- to 0.6 μg Hg/ml. Based on sample stability considerations, we have made the following recommendations:

1) Use 0.3M ICl or 4% $KMnO_4$/10% H_2SO_4 as the collecting liquid in place of a more dilute solution to increase the oxidative capacity of the sampling train and do not exceed the oxidation capacity of the solution during sampling.
2) If $KMnO_4/H_2SO_4$ is used as the collecting solution, prepare the reagent immediately before use.
3) Place 50 ml of the collecting reagent in the first impinger and at least 200 ml in the second and third impingers.
4) Place the contents of the entire sampling train in one jar and rinse all glassware with the collecting reagent.
5) Store the samples only in acid-washed glass jars with Teflon cap liners and process the samples as soon as possible after

collection.

6) At least one sample from each plant should be analyzed using the Method of Standard Additions regardless of the procedure used.

EXPERIMENTAL

Prior to conducting field tests, attempts were made to remove the interference of KI on the $SnCl_2$, but no practical way was found. One simple idea, decreasing the iodine monochloride concentration from 0.1M to 0.05M or less, was impractical because of the high oxidizable organic content of some of the stack gases that might be sampled. Attempting to collect more mercury by increasing the sampling time from two hours to six or eight hours was also impractical because of the high organic content and high moisture content of the stack gas. Consideration was also given to changing the reducing agent, but as shown by Melcher and Welz (5) an extensive evaluation would be required on numerous samples from many plants to ensure that another constituent of the stack gas or in the collecting liquid did not interfere with the analysis. For these reasons, it was decided to evaluate two procedures previously found to yield reliable results. In one procedure, the sample is collected in ICl and analyzed by NAA. In the other procedure the sample is collected in a $KMnO_4/H_2SO_4$ solution and analyzed by FAA (7).

Relative collection efficiency and sample stability were evaluated in four field tests. Collection efficiency was primarily evaluated by employing single-point, isokinetic sampling with two or more trains sampling simultaneously at essentially the same point in the stack. Stability of the mercury-containing samples was evaluated by:

1) analyzing the stack samples immediately after collection and also

at intervals spanning several months; 2) spiking stack samples with mercury and measuring its concentration as a function of storage time; 3) placing aliquots from some samples in 15% nitric acid and comparing their long-term stability to the original sample. During this testing program, the usefulness of placing a filter between the probe and first impinger and between the third and fourth impinger was also studied.

The basic sampling train consisted of four Greenburg-Smith impingers connected in series. The first, second and fourth field tests were conducted at a municipal sludge incinerator located in Ohio and the third test was conducted at one located in Maryland. The Ohio incinerator processed sludge from residential sources, while the Maryland incinerator processed sludge primarily from industrial sources. Both incinerators were equipped with wet scrubbers and had stack temperatures of about 65°C.

The first field test was conducted in April, 1978, the second in July 2978; the third in September 1978; and the fourth in May 1979. During the first test, the plant suffered a major process upset, and it was not possible to obtain a complete sampling run before the large amount of organic material in the stack completely exhausted the 0.1M ICl and 2% $KMnO_4$/10%H_2SO_4 mercury collecting solutions. Therefore, the test was repeated three months later at a time when plant operation was normal and the stack's oxidizable-organic material content was considerably lower. In this second test, four trains sampled simultaneously during each two-hour sampling run. Two of the trains contained 0.1M ICl; the others contained 2% $KMnO_4$/10%H_2SO_4. Only the color in the first impinger of all trains was bleached during sampling.

Four-train-sampling was also employed in the third test, but each train contained a different collecting solution, i.e., 0.1M ICl; 0.3M

ICl; 2% $KMnO_4$/10%H_2SO_4; and 4% $KMnO_4$/10%H_2SO_4. Four, 3-hour sampling runs were conducted. The oxidizable content of the stack gas was so minute that not even the first impinger solution was completely bleached during sampling.

These field tests indicated that the 4% $KMnO_4$/10%H_2SO_4 was the best collecting solution and flameless atomic absorption spectrometry the best analysis procedure. Thus, the fourth test was conducted only to determine the reserve capacity of this solution. In this study the paired-train testing was used. One train contained 0.5% $KMnO_4$/10%H_2SO_4 and the other contained 4% $KMnO_4$/10%H_2SO_4. Sampling was stopped just before the oxidative capacity of the train that contained 0.5% $KMnO_4$/10%H_2SO_4 was exhausted, giving a sampling time of approximately two hours.

Table 1. SAMPLING RESULTS AT SLUDGE INCINERATION PLANTS.

Test Date	Sampling Run	ICl Results (μg Hg/m^3)			$KMnO_4$ Results (μg Hg/m^3)						
		0.1M	0.1M	0.3M	0.5%	2%		2%		4%	
		NAA	NAA	NAA	FAA	FAA	NAA	FAA	NAA	FAA	NAA
7/78	1	58	42	-	-	35	-	35	-	-	-
	2	125	94	-	-	85	-	87	-	-	-
	3	65	55	-	-	50	60	48	67	-	-
	4	76	91	-	-	71	80	71	110	-	-
9/78	1	74	-	110	-	83	87	-	-	80	97
	2	128	-	116	-	134	121	-	-	129	121
	3	149	-	111	-	106	110	-	-	136	139
	4	90	-	107	-	115	107	-	-	141	142
4/79	1	-	-	-	49	-	-	-	-	51	-
	2	-	-	-	64	-	-	-	-	74	-

RESULTS AND DISCUSSION

The results from the three successful field tests are presented in Table 1. These investigations combined with sample stability and filter position studies conducted on stack samples yielded the following conclusions:

1) On the average the ICl/NAA results for the July 1978 test are slightly higher than the $KMnO_4$/NAA results. On the average, the ICl/NAA results for the September 1978 test are identical to the $KMnO_4$/FAA results. These observations indicate that the two collecting liquids have an equal collecting efficiency for mercury.

2) Within individual sampling runs, the agreement between two $KMnO_4$-containing trains is superior to that between two ICl-containing trains. This larger variation in the ICl results is likely due to the imprecision in the NAA procedure and is not due to sample instability or sample recovery errors. Thus, repeat analyses on the same sample showed that the precision of the $KMnO_4$/FAA procedure was much better than that for the ICl/NAA and $KMnO_4$/NAA procedure. For example, compare the following pairs of results in μg Hg/m^3 obtained on three samples analyzed by NAA (164, 134; 97, 83; 93, 81) to pairs of results obtained on three samples analyzed by FAA (80, 77; 83, 80; 129, 139).

3) The oxidizing capacity of the collecting solution should not be exceeded during testing or collection efficiency or sample stability may suffer. The samples themselves seem to be stable for at least several weeks as long as an oxidizing medium is maintained in the solution.

4) The suitability of locating a filter upstream of the impingers to remove some of the oxidizable material was initially studied in the first field test where it was found that the filter and probe temperature affected the amount of particulate collected on the filter. As the filter/probe temperature increased, the amount of collected material decreased. Due to the poor plant operation conditions during this period the stack gas contained large quantities of sooty particulate matter. When this test was repeated in May 1979, the plant was operating normally and filter temperature did not affect the particulate catch for the single, paired-train, sampling run conducted. The Method 5 train operated at 65°C measured a particulate concentration of 29.2 mg/m^3 and the Method 5 train operated at a 140°C measured a particulate concentration of 28.3 mg/m^3. The difference of 0.9 mg/m^3 is within the statistical variation expected for this type of test (8).

These results indicate that a filter located upstream of the impingers can assist in removing particulate matter but may not remove all of it if the plant is emitting sooty particulate. Furthermore, it would be unwise to attempt to simultaneously measure both particulate and mercury content using the same sampling train, because it is presently unknown whether any mercury collected on the filter would be lost during the filter-conditioning steps necessary to determine the particulate catch.

5) In the May 1979 test, glass-fiber filters followed the third impinger in each train to discover if mercury was passing through the train. At the conclusion of the sampling run, each filter was placed in a jar that contained 30 ml of 4% $KMnO_4$/10%H_2SO_4 solution and returned to the laboratory for mercury analysis. In all four trains a greyish material was found on

the filter, but less than 1% of the mercury collected in a train was found on the filter.

6) The brown MnO_2 precipitate that formed in the $KMnO_4$-containing trains during sampling never contained more than one percent of the mercury collected in the train.

7) The standards and samples must contain the same reagents for accurate FAA results and at least one sample should be subjected to the Method of Standard Additions (9).

Overall, the test results show that collection in ICl followed by NAA analysis or collection in $KMnO_4/H_2SO_4$ followed by FAA or NAA analysis will yield acceptable results. The FAA procedure is preferred from the view of cost of analysis (NAA can cost as muc as $100 per sample and the quartz vials must be sealed with an oxy-hydrogen torch), precision and methodology presently there is no standardized method for mercury analysis by NAA). On the other hand, the ICl/NAA procedure is preferred from the view of sample stability, (once placed in the vial, sample stability does not affect the results) reagent stability, (the $KMnO_4/H_2SO_4$ solution must be prepared within 12 hours of use) and sample recovery ($KMnO_4$ decomposes during sampling and storage to give a brown precipitate and a brown ring on the impinger wall that must be removed with 8N HCl.). Before NAA can be used routinely, it must be standardized in the following areas: sample volume, quartz vial purity, irradiation time, flux strength, number of analyses per sample, time interval between irradiation and counting, counting time, wavelength(s) to be used for counting purposes, and number and concentration of standard samples to be processed with source samples.

Regardless of the collecting solution used, the oxidizing capacity of the collecting reagent must not become exhausted during sampling. Thus,

even though samples appear to be stable for at least several weeks, they should be processed within several days of collection. For NAA processing involves placing the sample in a quartz vial. For FAA processing means the complete analysis. Samples should be processed as soon after collection as possible, because dilute mercury solutions are notoriously unstable. Findlay (7) reported that a 10 µg Hg/ml (in 1% HNO_3) standard solution was stable for about one week, but mercury solutions containing 10 ng/ml in a completely reduced permanganate solution were stable for less than one hour. Feldman (10) reported that solutions containing below 0.025 µg/ml were stable for less than 24-hours even in 5% nitric acid. He also noted that the stability of dilute solutions was affected by suspended particulate matter and by storage container material, i.e., solutions stored in polyethylene bottles were much less stable than those stored in glass bottles.

SECTION 2

SLUDGE ANALYSIS METHOD

INTRODUCTION

In March 1977, the Quality Assurance Branch (QAB) of the Environmental Monitoring and Support Laboratory, conducted a collaborative test of EPA Method 105 (1). In the collaborative test ten laboratories analyzed portions of grab samples of dewatered sludge taken from three sludge treatment plants. (Grab rather than composite samples were used to minimize the effect of sample non-homogeneity on the results, since Method 105 was concerned only with sample analysis and not sample collection.). Each 150-g grab sample was manually mixed for 15 minutes and divided into 10-g portions. Each laboratory received a 10-g portion from each plant, dried each sample and then digested and analyzed 0.2 g portions in triplicate as described in EPA Method 105 (1). To provide an alternate determination of Hg content, an EPA laboratory analyzed a portion of each grab sample in duplicate using neutron activation analysis (NAA).

The results of this collaborative test clearly indicate that for a given sample between-laboratory and, at times, with-laboratory, agreement was poor (Table 2). A statistical analysis of the results indicated that non-homogeneity in mercury concentration was a significant cause of the within-sample variation in at least two of the three samples - an indication that hand-mixing was an ineffective way to homogenize sludge samples for mercury analysis. This finding was important because Method 105 normally would be used on a composite sludge sample composed of eight grab samples, and the regulations did not specify any definitive sludge mixing procedure

for this composite sample.

The following study was done to develop and validate a method to ensure that sludge samples were properly homogenized before chemical analysis. This study used sludge samples collected at three sewage sludge incinerators. The sample weight and sampling interval were two major parameters investigated in detail.

SUMMARY AND CONCLUSIONS

Dewatered sewage sludge samples cannot be reliably homogenized, at least for mercury (Hg) analysis by manual mixing alone. However, effective homogenization can be obtaied using a commercially available mortar mixer. One unexpected result from the study was the observation that the mercury content of dewatered sludge entering the conveyor line varied in an unpredictable way with time. For example, it was found that a 27 kg (60 lb) bulk sewage sludge sample composed of grab samples taken at 5 minute intervals could have a mercury content statistically different from that in a similar weight sample collected in the same period composed of grab samples collected at 10 minute intervals. Individuals collecting sludge samples for trace element analysis should consider this factor when sampling the sludge conveyor line.

EXPERIMENTAL

The collaborative test results indicated that even within a small grab sample of sludge there could be a non-homogeneous distribution of mercury. Therefore, it seemed likely, that a more extreme non-homogeneous distribution would exist on the sludge conveyor line itself. Thus, the larger the bulk sample taken from the sludge conveyor line, the more representative the

TABLE 2. COLLABORATOR RESULTS ON SEWAGE SLUDGE SAMPLES

(μg Hg/g DRIED SLUDGE).

Sample	NAA Results	Method 105 Results									
		Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10
1	1.8	3.8	2.8	2.8	0.66	1.0	3.1	1.4	1.2		0.33
	3.9	3.3	2.7	2.8	0.82	1.5	3.1	1.2	1.6		0.45
		0.87	2.8	3.7	0.91	1.0	3.5	1.2	1.4		0.63
2	3.0	4.1	2.5	2.7	0.57	1.1	1.8	10.	1.5		0.18
	2.2	2.7	2.3	2.9	0.48	1.6	2.0	12.	1.4		a
		1.0	2.3	3.6	0.45	5.1	2.2	13.	1.3		0.94
3	2.3	3.8	3.0	2.6	0.71	2.0	3.3	2.3	2.7		0.49
	2.4	3.9	2.9	2.8	1.1	3.8	2.2	1.9	2.7		0.82
		0.79	3.0	3.5	1.6	2.2	3.8	2.7			

*No Hg detected.

mercury analysis should be, provided of course that this bulk sample could be thoroughly blended and homogenized before analysis.

For this reason, it was decided to develop and evaluate a procedure that could quickly but effectively homogenize large amounts of sewage sludge. When various sludge mixing procedures were evaluated by adding zinc oxide to dewatered sludge and analyzing for mercury and zinc as a function of mixing time, it was found that a 57 liter (2 ft^3) capacity wheelbarrow-type commercial mortar mixer rotating at 30 rpm for at least 30 minutes would effectively mix sludge samples. Mixing times less than 30 minutes were found to be inadequate.

Sludge Sampling

The effectiveness of this new mixing technique was verified using time-composite dewatered sludge samples from three sludge treatment plants. Simultaneously a study was conducted to determine the optimum sampling interval for collecting samples from the conveyor line for the time-composite (bulk) sample. To accomplish this, the sludge conveyor line was sampled so that over an eight hour interval, 27-kg bulk samples comprised of grab samples taken at different sampling intervals were collected. For example, one bulk sample would be composed of 0.3-kg grab samples collected at 5-minute intervals and another would be composed of 1.0-kg samples collected at 15-minute intervals. Sampling intervals of 5,- 10,- 15,- 20,- 25,- 30,- and 60-minutes were used in this study, although not all of these intervals were used at every plant.

Sludge Analysis

Each 27-kg sample was returned to the laboratory where the entire sample was placed in the mortar mixer and mixed for at least 30 minutes at 30 rpm. Two to four, 500-ml samples were then withdrawn from the mixer and each 500-ml sample was blended in a 2-liter Waring-type blender for two minutes. Three to five, 20-ml sludge samples were then withdrawn from the blender, put into separate tared 125-ml Erlenmeyer flasks and the flasks reweighed to obtain the exact weight of sludge added. Twenty-five ml of aqua regia was added to each sample and the sample was digested at low temperature for 30 minutes on a hot plate, cooled, filtered through S and S No. 588 filter paper, diluted to 100 ml and analyzed for Hg using the apparatus described by Mitchell and Midgett (4) and the analytical procedure summarized below.

A 5- to 25-ml aliquot of the digested sample was added to 25-ml of distilled, deionized water in the aeration bottle. Three drops of Baker Antifoam B Silicon Emulsion were added, followed in sequence by 5-ml of 15% (V/V) nitric acid and 5-ml of 5% (by weight) potassium permaganate. The solution was then mixed well using a magnetic stirring bar. A solution, prepared by dissolving 12 g of sodium chloride and 12 g of hydroxylamine sulfate in 100 ml of distilled, deionized water, was then added in 5-ml aliquots until a colorless solution was obtained. Five ml of 10% (by weight) stannous chloride (4) was added to the aeration cell and the mercury aerated into the atomic absorption cell using nitrogen as the purge gas. Selected samples were also spiked and reanalyzed by the Method of Standard Additions (9) to confirm the accuracy of the original analysis.

RESULTS AND DISCUSSION

Table 3 summarizes the results obtained at each sludge treatment plant in relation to: frequency of sludge removal from the conveyor belt over an eight-hour interval (bulk sample); number of 500-ml samples withdrawn from the mortar mixer; number of aliquots analyzed from each blended 500-ml sample; and the grand mean (μg Hg/g dried sludge) for each bulk sample. During this study, a total of 48, 500-ml samples were taken from 18 bulk (27-kg) samples and at least three analyses were performed on each 500-ml sample after blending.

A comparative statistical analysis on all results showed that: 1) all 20-ml aliquots from a 500-ml sample were statistically identical; 2) all 500-ml aliquots from a bulk sample were statistically identical with the exception of one sample from Plant 1; and, 3) bulk samples from the same plant were not always statistically identical. For example, the 10- and 20 minute interval samples from Plant 3 (July 1978) are statistically different from the other four bulk samples. Analogously, the 5-, 15-, and 30-minute interval samples from Plant 1 are statistically the same, but the 60-minute interval sample is statistically different from the 5- and 15-minute interval samples.

These results show that the bulk sludge samples were effectively homogenized but that the actual Hg content of the bulk samples was affected in an unpredictable manner by the sampling frequency. Although the cause of this time variation remains unidentified, it might originate from each plant having at least two processes contributing sludge to the conveyor belt at the same time but on an intermittent basis, i.e., sludge would be deposited at 1- to 5-second intervals. Further, the volume of sludge deposited on the conveyor line at any one time by each process also

varied from minute-to-minute. If this is the origin, then perhaps a similar variation will occur when a sludge line is sampled to determine other trace elements present. Since this variation would result from the process itself, the simplest way to minimize its effect on analytical results would be to collect a large bulk sample composed of many grab samples, e.g., take grab samples no further than 15 minutes apart.

Although undesirable, this rapid variation in mercury content of the sludge line can probably be tolerated, since the objective of the sludge analysis is only to determine if a stack test is necessary.

SECTION 3

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9. Klein, R., and C. Hach. Standard Additions, Uses and Limitations in Spectrophotometric Analysis. Amer. Lab. 9:21-27 (1977).

10. Feldman, C. Preservation of Dilute Mercury Solutions. Anal. Chem. 46:99-102 (1974).

TABLE 3. EFFECT OF SAMPLING FREQUENCY ON MERCURY RESULTS

Sampling Date	Plant No.	No. of 500-ml Samples from Each Bulk Sample	No. of 20-ml Aliquots from Each 500-ml Sample	Mercury Content (µg Hg/g dried sludge) in Each Bulk Sample						
				5-min[a]	10-min[a]	15-min[a]	20-ml[a]	25-ml[a]	30-ml[a]	60-ml[a]
1/78	1	2	5	1.28	*	1.19	*	*	1.57	1.87
[illegible]/78	2	2	5	2.88	*	2.95	*	*	2.61	3.33
4/78	3	2	5	2.65	*	2.12	*	*	2.92	3.25
7/78	3	4	3	4.78	4.01	4.82	5.40	4.46	4.50	*

[a]Sampling interval used in collecting the 8-hour bulk sample.

*Not done at this plant.

APPENDIX A

METHOD TO DETERMINE PARTICULATE AND GASEOUS MERCURY EMISSIONS FROM SEWAGE SLUDGE INCINERATOR STACKS

1. Principle and Applicability

1.1 Principle. Particulate and gaseous mercury emissions are withdrawn isokinetically from the source and collected in acidic potassium permanganate ($KMnO_4$) solution. The mercury collected (in the mercuric form) is reduced to elemental mercury, which is then aerated from the solution and passed into an optical cell in an atomic absorption spectrometer, where the maximum absorbance at 253.7 nm is measured.

1.2 Applicability. This method is applicable for the determination of particulate and gaseous mercury emissions when the carrier gas stream is principally air, flowing in a duct or stack.

2. Range and Sensitivity

2.1 Range. As written, the analytical method is applicable to source test samples that contain (after initial dilution) between 20 and 800 ng Hg/ml Samples containing in excess of 800 ng Hg/ml can be analyzed by this method if diluted. Samples containing less than 20 ng Hg/ml per milliliter should not be analyzed by this method because they are stable for less than 24 hours.

2.2 Sensitivity. This depends on the recorder/spectrometer combination selected.

3. Interfering Agents

3.1 Sampling. Excessive oxidizable-organic matter in the stack gas will cause premature depletion of the $KMnO_4$ solution, thereby preventing further collection of mercury.

3.2 Analysis. Condensation of water vapor on the optical cell windows produces a positive interference.

4. Precision

4.1 Within-Laboratory Standard Deviation. The estimated within-laboratory standard deviation of the procedure in the concentration range of 50 to 130 µg Hg/m^3 is 4.8 µg Hg/m^3. This estimate is based on eight, paired-train tests conducted during the study to develop and validate this method.

5. Apparatus

5.1 Sampling Train. A schematic diagram of the sampling train is shown in Figure 1. Complete construction details are given in APTD-0581 (Citation 4, Section 11); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train

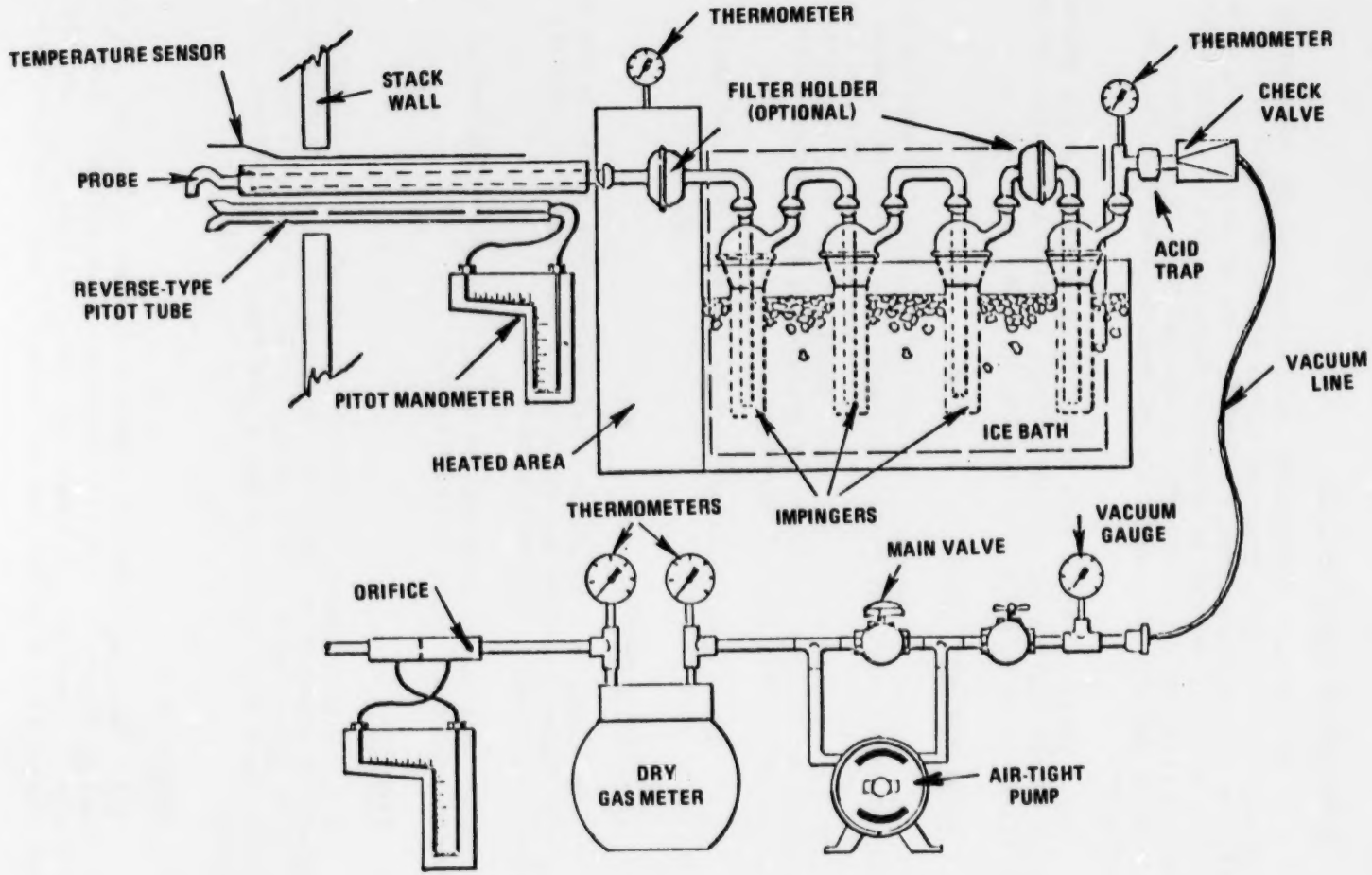

Figure 1. Mercury sampling train.

(Figure 1), see the following subsections. Note that use of a flexible line between the probe and the first impinger is unacceptable.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (Citation 5, Section 11). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt its operating and maintenance procedures, unless otherwise specified. The sampling train consists of the following components:

5.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be $\leq 30°$ and the taper shall be on the exterior to preserve a constant internal diameter. The probe nozzle shall have a button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing; other materials of construction may be used, subject to approval of the Administrator.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) inner diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be properly calibrated.

5.1.2 Probe Liner. Borosilicate or quartz glass tubing. A heating system capable of maintaining a gas temperature at the probe exit during sampling of 120 ± 14°C (248 ± 25°F) may be used to prevent water condensation. If a filter is used ahead of the impingers, use of the probe heating system is mandatory. Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-058 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable. NOTE: Metal probe liners are unacceptable.

5.1.3 Pitot Tube. Type-S, (as described in Section 2.1 of Method 2, Citations 1,2, Section 11) or other devices approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as described in Section 4 of Method 2.

5.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in Section 2.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

5.1.5 Impingers. Four Greenburg-Smith impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first, third and fourth impingers may be modified by replacing the tip with a 13 mm (0.5 in.) ID glass tube extending to 13 mm (0.5 in.) from the bottom of the flask.

5.1.6 Acid Trap. Mine Safety Appliances* Air Line Filter, Catalogue Number 81857, with acid absorbing cartridge and suitable connections, or equivalent.

5.1.7 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in (Figure 1) other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

5.1.8 Filter. Glass fiber, Gelman Spectrograde or equivalent filter.

5.1.9 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice-versa for elevation decrease.

5.1.10 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, (See Citation 1, Section 11). The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. However, if the temperature sensor is attached in the field, it must be placed in an interference-free arrangement with respect to the pitot tube opendings (see Method 2, Figure 2-7). As a second alternative, provided that a difference of not more than 1 percent in the average velocity measurement is introduced, the temperature gauge need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

5.2 Sample Recovery.

5.2.1 Leakless Glass Sample Bottles. 1000 ml and 100 ml with Teflon-lined caps.

5.2.2 Graduated Cylinder. 250 ml.

5.2.3 Plastic Container. Approximately 350 ml.

*Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.

5.2.4 Balance. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances are suitable for use here.

5.2.5 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

5.2.6 Funnel. Glass, to aid in sample recovery.

5.3 Analysis.

5.3.1 Atomic Absorption Spectrometer. Perkin-Elmer 303, or equivalent, containing a hollow cathode mercury lamp and capable of containing the optical cell described in Section 5.3.2.

5.3.2 Optical Cell. Cylindrial-shape with quartz end windows and having the dimensions shown in Figure 2. The cell is wire-wound with approximately 2 meters of 24 gauge nichrome heating wire and wrapped with asbestos insulation tape or equivalent; the wires must not touch one another.

5.3.3 Aeration Cell. Constructed according to the specifications in Figure 3. A glass frit is not an acceptable substitute for the blown glass bubbler tip shown in Figure 3.

5.3.4 Recorder. Matched to the output of the spectrometer described in Section 5.3.1.

5.3.5 Variac. To vary the voltage on the optical cell from 0 to 40 volts.

5.3.6 Hood. For venting optical cell exhaust.

5.3.7 Flow Metering Valve.

5.3.8 Flow Meter. Rotameter or equivalent, capable of measuring a gas flow of 1.5 liters/minute.

5.3.9 Nitrogen Cylinder. Equipped with a single stage regulator.

5.3.10 Connecting Tubing. All connecting tubing between the solution cell and the optical cell shall be made of glass (ungreased ball and socket connections are recommended). Tygon tubing, other types of flexible tubing, and metal tubing are not acceptable substitutes. Teflon, steel, or copper tubing should be used between the nitrogen tank and the flow meter valve (5.3.7). Tygon, gum or rubber tubing may be used between the flow metering valve and the solution cell.

5.3.11 Flow Rate Calibration Equipment. Bubble flowmeter or wet test meter for measuring a gas flow rate of 1.5 liter/minute to within $\pm$ 0.1 liter/minute.

5.3.12 Volumetric Flasks. Class A with penny head standard taper stoppers; 100 and 500 ml.

5.3.13 Volumetric Pipets. Class A; 1, 2, 3, 4 and 5, 10, 20 ml.

5.3.14 Graduated Cylinder. 25 ml.

5.2.15 Magnetic Stirrer. General purpose laboratory type.

5.3.16 Magnetic Stirring Bar. Teflon coated.

5.3.17 Filter. Whatman No. 40 or equivalent.

6. Reagents

6.1 Stock Reagents.

6.1.1 Water. Distilled, meeting ASTM specifications for Type I Reagent Water - ASTM Test Method D-1193-72. The $KMnO_4$ test for oxidizable organic matter may be eliminated when high concentrations of organic matter are not expected to be present. This water must be used in all dilution and solution preparations.

6.1.2 Nitric Acid, Concentrated. American Chemical Society (ACS) reagent grade, or equivalent.

6.1.3 Sulfuric Acid, Concentrated. ACS reagent grade, or equivalent.

6.1.4 Hydrochloric Acid, Concentrated. ACS reagent grade, or equivalent.

6.1.5 Potassium Permanganate. ACS reagent grade, or equivalent.

6.1.6 Sodium Chloride. ACS reagent grade, or equivalent.

6.1.7 Hydroxylamine Sulfate. ACS reagent grade, or equivalent.

6.1.8 Tin(II) Chloride (Crystal). Baker Analyzed Reagent Grade or any other brand of analyzed reagent grade tin (II) chloride that will give a clear solution when dissolved as described in Section 6.3.3. Tin (II) sulfate (crystal) of the same purity may be substituted for the Tin (II) chloride, provided it gives a clear solution.

6.1.9 Mercury(II)Chloride. ACS reagent grade, or equivalent.

6.1.10 Mercury Stock Solution (1 mg Hg/ml). Completely dissolve 0.1354 g of mercury (II) chloride in 75 ml of distilled water, add 10 ml of concentrated nitric acid and adjust the volume to 100 ml with distilled water. Mix thoroughly. This solution should remain stable for at least one month.

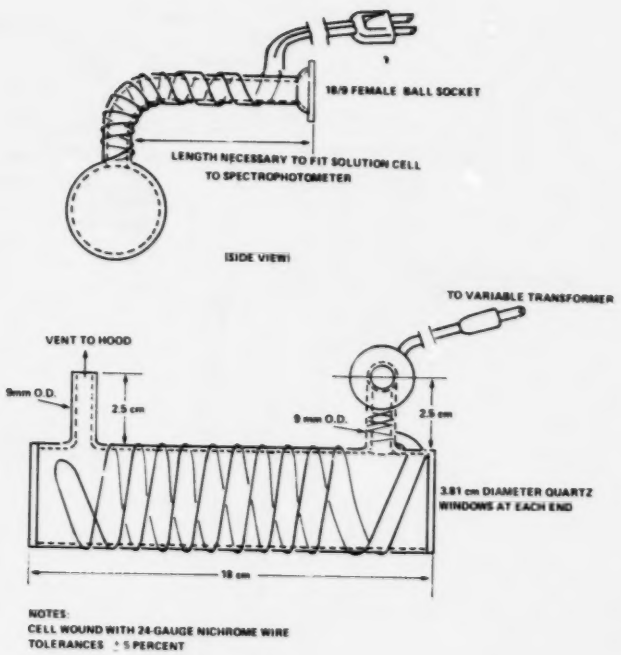

Figure 2. Optical cell.

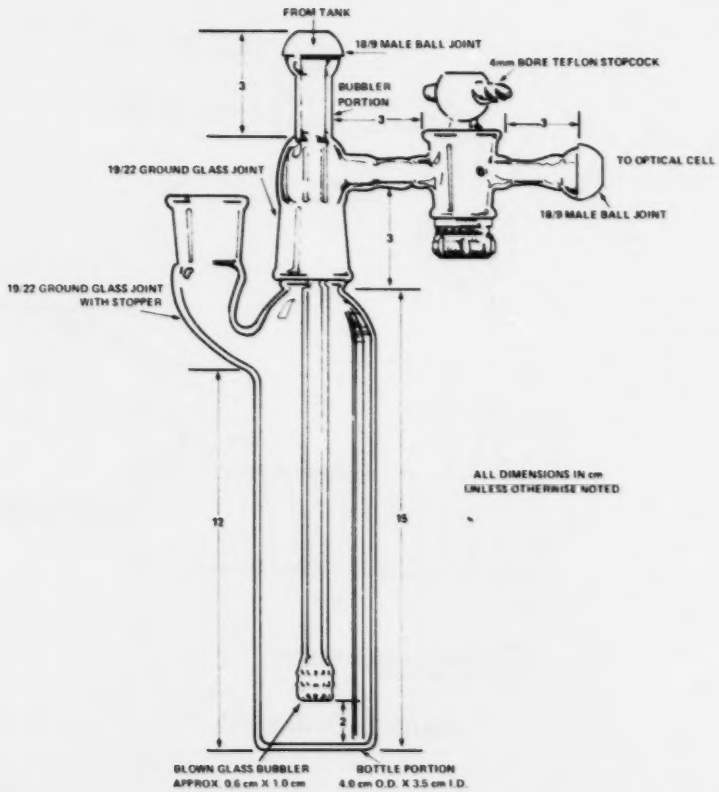

Figure 3. Aeration cell.

6.1.11 Sulfuric Acid Solution (10 Percent V/V). Dilute 100 ml of concentrated sulfuric acid to 1000 ml using distilled water.

6.1.12 Nitric Acid Solution (15 Percent V/V). Dilute 15 ml of concentrated HNO_3 to 100 ml using distilled water.

6.1.13 Hydrochloric Acid (8N). Dilute 67 ml of concentrated HCl to 100 ml using distilled water.

6.2 Sampling Reagents.

6.2.1 Water. Same as 6.1.1.

6.2.2 Absorbing Solution, 4% $KMnO_4$. Prepare fresh daily by dissolving 40 g of $KMnO_4$ in sufficient 10% (V/V) H_2SO_4 to make one liter. The solution should be prepared only in glass bottles to prevent degradation.

6.2.3 Wash Acid. 1:1 V/V Concentrated Nitric Acid and Water.

6.2.4 Silica Gel. Indicating type, 6- to 16-mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received.

6.3 Analysis Reagents.

6.3.1 Intermediate Mercury Standard Solution, 10 µg Hg/ml. Prepare fresh weekly. Pipet a 5.0 ml aliquot of the mercury stock solution (6.1.11) into a 500-ml volumetric flask and add 20 ml of 15% (V/V) HNO_3 solution. Adjust the volume to 500 ml using distilled water. Thoroughly mix the solution.

6.3.2 Working Mercury Standard Solution, 200 ng Hg/ml. Prepare fresh daily. Pipet a 5.0 ml aliquot from the "Intermediate Mercury Standard Solution" into a 250-ml volumetric flask. Add 5 ml of the absorbing solution and 5 ml of 15% (V/V) HNO_3. Adjust the volume to 250 ml with distilled water. Mix thoroughly.

6.3.3 Sodium Chloride-Hydroxylamine Sulfate Solution. Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml. Hydroxylamine hydrochloride may replace hydroxylamine sulfate.

6.3.4 Tin(II) Chloride Solution. Prepare daily and keep sealed when not being used. Completely dissolve 20 g of tin(II) chloride (or 25 g of tin(II) sulfate) in 25 ml of concentrated hydrochloric acid. Bring the total volume to 250 ml using distilled water. Other strong acids such as nitric acid and sulfuric acid are not to be substituted for the hydrochloric acid.

7. Procedure

7.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, field personnel should be trained and experienced with the test procedures. Sampling guidelines are given in the following sections. These guidelines are generally applicable; however, source alterations such as stack extensions or expansions often are required to ensure the best possible sample site. Note also that since mercury is a hazardous pollutant, care should be taken to minimize exposure to it. Finally, since the total quantity of mercury to be collected is generally small, the method must be carefully applied, to prevent contamination or loss of sample.

7.1.1 Pretest Preparation. All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

Weigh to the nearest 0.5 g several 200 to 300 g portions of silica gel in air-tight containers. Record the total weight of the silica gel plus contained, on each container. Alternatively, the silica gel may be weighed directly into its impinger just prior to train assembly.

7.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 (Citation 1, Section 11), or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2, (Citation 1, Section 11). It is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Reference Method 4, (Citation 1, Section 11), or its alternatives to decide isokinetic sampling rate settings. Determine the stack gas dry molecular weight, (See Method 2, Section 3.6).

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to isokinetically maintain a sampling rate of between 14 and 28 lpm (0.5 and 1.0 cfm). During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2, Citation 1,2, Section 11).

Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Samples shall be taken over periods of time as are necessary to accurately determine the maximum emissions occurring in a 24-hr period. In the case of cyclic operations, sufficient tests shall be made to allow accurate determination of the emissions that occur over the duration of the cycle. A minimum sample time of 2 hours is recommended. In some instances, high oxidizable-organic content of the stack gas may make it impossible to sample for the desired minimum time. This is

indicated by complete bleaching of the purple color of the permanganate solution. In these cases, a sample run may be divided into two or more subruns to ensure that the absorbing solution is not depleted.

7.1.3 Preparation of Sampling Train. Prior to assembly, clean all glassware (probe, filter holder [if used], impingers, and connectors) by rinsing with wash acid, tap water, 8N HCl, tap water, and finally distilled water. Place 50 ml of absorbing solution in the first impinger; place 100 ml of absorbing solution in the second and third impingers and place approximately 200 g of preweighed silica gel in the fourth impinger. Care should be taken to prevent the absorbing solution from contacting any greased surfaces.

Using a tweezer, place a filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed to prevent the sample gas stream from circumventing the filter. (Note: The use of a filter is optional and if one is used, it must be stored in contact with the absorbing solution after use. It may not be desiccated before analysis.)

Install the selected probe liner using a Viton A O-ring when stack temperatures are less than 260° (500°F) and an asbestos string gasket for higher temperatures. (See APTD-0576 for details.) Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat resistant tape or another method to denote the proper distance into the stack or duct for individual sampling points. Assemble the train as shown in Figure 1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease.

After the sampling train has been assembled, set the probe and if applicable, the filter heating system at the desired operating temperature. Allow time for the temperature to stabilize. Place crushed ice around the impingers.

7.1.4 Leak-Check Procedures. Follow the leak-check procedures outlined in Method 5, Sections 4.1.4.1 (pretest leak-check), 4.1.4.2 (leak-checks during sample run), and 4.1.4.3 (post-test leak-check). (See Citations 1,2, Section 11.)

7.1.5 Mercury Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified and a temperature around the filter (if applicable) of 120 $\pm$ 14°C (248 $\pm$ 25°F).

For each run, record the data required on a data sheet such as the one shown in Figure 4. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings required by Figure 4 at least once at each sample point during each time increment and additional readings

PLANT _____

LOCATION _____

OPERATOR _____

DATE _____

RUN NO. _____

SAMPLE BOX NO. _____

FILTER BOX NO. _____

METER ΔH@ _____

C FACTOR _____

PITOT TUBE COEFFICIENT, C_p _____

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE _____

BAROMETRIC PRESSURE _____

ASSUMED MOISTURE, % _____

PROBE LENGTH, m (ft) _____

NOZZLE IDENTIFICATION NO. _____

AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) _____

PROBE HEATER SETTING* _____

LEAK RATE, m^3/min (cfm) _____

PROBE LINER MATERIAL _____

STATIC PRESSURE, mm Hg (in.Hg) _____

FILTER NO.* _____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in. Hg)	STACK TEMPERATURE (T_S) °C (°F)	VELOCITY HEAD (ΔP_S),	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H_2O (in. H_2O)	GAS SAMPLE VOLUME m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		FILTER HOLDER* TEMPERATURE, °C (°F)	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET °C (°F)	OUTLET °C (°F)		
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

*IF APPLICABLE

Figure 4. Mercury field data.

when significant changes (20 percent variation in velocity head) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling deposited material. To begin sampling, remove the nozzle cap and verify that the probe and, if applicable, filter are at the proper temperature and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.85 + 0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29 + 4. APTD-0576 details the procedure for using the nomographs if C_p and M_d are outside the above stated ranges.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent impinger liquid from being forced backward. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross-section, as required by Method 1 (Citation 1,2, Section 11) or as specified by the Administrator. To minimize the chance of extracting deposited material be careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes.

During the test run, add ice and, if necessary, salt to maintain a temperature of less than 20°C (68°F) at the silica gel outlet. Also, periodically check the level and zero of the manometer.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, when equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check (see Section 7.1.4). Also, leak-check the pitot lines as described in Section 3.2 of Method 2, (Citations 1,2, Section 11). The lines must pass this leak-check in order to validate the velocity head data.

7.1.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (Section 6.11 of Method 5, Citations 1,2, Section 11) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

7.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off any external particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling since this would create a vacuum and draw liquid out from the impingers.

Before moving the train to the cleanup site, remove the probe, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate present. Wipe off silicone grease from the impinger (or filter holder) inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the entire sampling train to the cleanup area. This area should be clean, protected from the wind, and free of mercury contamination. (Ambient air in laboratories located in the immediate vicinity of mercury-using facilities is normally not free of mercury contamination.)

Inspect the train prior to and during disassembly and note any abnormal conditions. Note: All glass storage bottles and the graduated cylinder must be precleaned as described in Section 7.1.3. Treat the samples as follows:

Container No. 1. Measure the liquid in the first three impingers to within $\pm$ 1 ml by using a graduated cylinder. Record the volume of liquid present (e.g., see Figure 5-3 of Reference Method 5, (Citation 1, Section 11). This information is required to calculate the moisture content of the effluent gas. Place the contents of the first three impingers into a 1000 ml glass sample bottle.

Taking care to see that dust on the probe or other exterior surfaces does not contaminate the sample, quantitatively recover the mercury (and any condensate) from the probe nozzle, probe fitting, probe liner and impingers by rinsing these components with a total of 250 to 400 ml of fresh absorbing solution. Add all washings to the 1000 ml sample bottle. Remove any residual brown deposits on the glassware using the minimum amount of 8 N HCl required and add this HCl rinse to the 1000 ml sample bottle.

After all washings have been collected in the sample container, tighten the lid on the container so that leakage will not ocur when

it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

Container No. 2. If a filter was used in the sampling train carefully remove it from the holder and place it in a 100 ml jar equipped with a teflon-lined cap. Add 20-40 ml of 4% $KMNO_4$/10% H_2SO_4 to the bottle and cap.

Container No. 3. Place an unused filter in a 100 ml bottle equipped with a teflon-lined cap. Add 20-40 ml of 4% $KMNO_4$/10% H_2SO_4 to the bottle and cap. This will serve as a filter blank.

Container No. 4. For a blank, place 500 ml of 4% $KMnO_4$/10% H_2SO_4 in a 1000 ml sample bottle and seal the container.

Container No. 5. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

8. Calibration and Standards.

8.1 Aeration System Assembly. Assemble the aeration system as shown in Figure 5. Flow Calibration. Set the outlet pressure on the nitrogen cylinder regulator to a minimum pressure of 500 mm Hg (10 psi) and use the flow meter valve and a bubble flow meter or wet test meter to obtain a flow rate through the solution cell of 1.5 $\pm$ 0.1 liters/min. After flow calibration is complete, remove the bubble flow meter from the system.

8.2 Optical Cell Heating System Calibration. Using a 25 ml graduated cylinder, add 25 ml of distilled water to the bottle section of the aeration cell and attach the bottle section to the bubbler section of the cell. Attach the solution cell to the optical cell, and while aerating at 1.5 liters/minute, determine the minimum Variac setting necessary to prevent condensation in the optical cell and in the connecting tubing. (This setting should not exceed 20 volts.)

8.3 Preparation of Glassware For Use in Analysis. Before use, all glassware, both new and used, should be brushed with soap and water, liberally rinsed with tap water, soaked for one hour in a 1:1 nitric acid/water solution and then rinsed with distilled water.

The rate at which elemental mercury is released from a solution is affected by the solution temperature. Consequently, the shape of the absorption curve (area) and the point of maximum absorbance (peak height) are affected by the solution temperature. Therefore, to obtain reproducible results, it is important to bring all solutions to room temperature before use.

8.4 Analytical System Calibration for Analysis.

8.4.1 Spectrophotometer and Recorder Calibration. Set the spectrophotometer wavelength dial to 253.7 nm and make certain the optical cell is at the minimum temperature that will prevent water condensation from occurring. Then set the recorder scale as follows: Using a 25 ml graduated cylinder, add 25 ml of distilled water to the aeration cell bottle and pipet a 5.0 ml aliquot of the working mercury standard solution into the aeration cell. (NOTE: The mercury-containing solution should always be added to the aeration cell after the 25 ml of distilled water.) Place a Teflon-coated stirring bar in the bottle. Add 5 ml of 4% $KMnO_4$/10% H_2SO_4 followed by 5 ml of 15% nitric acid and 5 ml of 5% potassium permanganate to the aeration bottle and mix well. Now, attach the bottle section to the bubbler section of the aeration cell and make certain that: (1) the aeration cell exit arm stop-cock (Figure 3) is closed (so that mercury will not prematurely enter the optical cell when the reducing agent is being added); and (2) there is no flow through the bubbler. Add 5 ml of sodium chloride-hydroxylamine sulfate solution to the aeration bottle through the side arm and mix. If the solution does not clear, add additional sodium chloride hydroxylamine sulfate in 1-ml increments until the solution is colorless. Now add 5 ml of 10% stannous chloride solution to the aeration bottle through the side arm and immediately stopper the sidearm. Stir the solution for 15 seconds, turn on the recorder, open the aeration cell exit arm stopcock and then immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard and set this value to read 90 percent of the recorder full scale.

8.4.2 Calibration Curve. Repeat the procedure in Section 8.4.1 using 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0-ml aliquots of the working standard solution. Repeat this procedure on each aliquot size until two consecutive peaks agree within 3 percent of their average value. The final amount of mercury in the aeration bottle for the 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0-ml aliquots will be 0, 200, 400, 600, 800 and 1000 ng, respectively. NOTE: To prevent mercury carry-over from one sample to another, it is important that the nitrogen tank valve remains open and that the aeration cell remains connected to the optical cell until the recorder pen has returned to the baseline to ensure that all mercury has been purged from the system. After separating the bottle and bubbler sections of the aeration bottle, place the bubbler section into a 600-ml beaker containing approximately 400 ml of distilled water to remove all traces of the reducing agent. In addition, to prevent the loss of mercury prior to aeration, all traces of the reducing agent (tin(II)chloride) must be removed between samples. This is accomplished by washing with distilled water, however, washing the aeration cell parts with concentrated hydrochloric acid is necessary if any of the following conditions occur: (1) a white film appears on any inside surface of the solution cell; (2) a sudden change is observed in the cali-

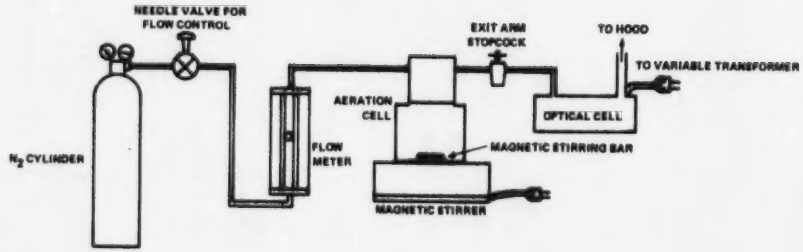

Figure 5. Schematic of the aeration system.

bration curve; (3) reproducible results are not obtained on replicate samples; or, (4) after a sample with an abnormally high mercury content is analyzed.

Subtract the averaged peak height of the solution blank (0.0-ml aliquot) - which should be less than 2 percent of the recorder full scale - from the averaged peak heights of the 1.0-ml, 2.0-ml, 3.0-ml, 4.0-ml and 5.0-ml aliquot standards. (If the blank absorbance is greater than 2 percent of full-scale, the probable cause is mercury contamination of a reagent or carry-over of mercury from a previous sample.) Plot the corrected peak height of each standard solution versus the corresponding total weight of mercury in the aeration cell and draw the best fit straight line. This plot should pass either through the origin, or through a point no further from the origin than $\pm$ 2 percent of the recorder full-scale. If a discovery occurs, check for nonlinearity of the curve and for incorrectly prepared standards.

8.5 Analysis of Stack Samples.

8.5.1 Container No. 2. (Filter). Place contents, including filter into a 250 ml beaker and heat this on a steam bath until most of the liquid has evaporated. Do not take to dryness! Add 20 ml concentrated nitric acid to the beaker, cover it with a watch glass and heat it on the steam bath for 2-hrs. Remove and filter the solution through Whatman No. 40 filter paper. Save the filtrate for analysis for mercury. Discard the filter.

8.5.2 Container NO. 3. (Filter Blank). Treat as described in Section 8.5.1.

8.5.3 Container No. 1. (Probe/Impinger Samples) Filter the impinger contents through Whatman No. 40 rapid filter paper to remove the brown MnO_2 precipitate. Wash the filter with 50 ml of 4% $KMnO_4$/10% H_2SO_4 solution and add this wash to the filtrate. Save the filtrate for analysis for mercury. Discard the filter.

8.5.4 Container No. 4. (Absorbing Solution Blank). Treat as described in Section 8.5.3. Combine this filtrate with the filtrate from Container No. 3 (Section 8.5.2) to serve as the sample blank and treat as described in Section 8.5.5.

8.5.5 Analysis. Combine the filtrates from Containers No. 1 and No. 2, mix and dilute to a known volume with distilled water. Repeat the procedure used to establish the calibration curve (Sections 8.4.1, 8.4.2) using an appropriate sized aliquot (1-10 ml) from the stack sample. (NOTE: If the 10-ml sample is below the detectable limit, a larger aliquot should be used (up to 20-ml), but the volume of water added to the aeration cell should be decreased accordingly to prevent the solution volume from exceeding the capacity of the aeration bottle. If the peak maximum of a 1.0-ml aliquot of sample is off scale further dilution of the original sample must be done to bring the mercury concentration into the calibration range of the spectrophotometer.

Analyze successive aliquots of each sample and the field sample blank until two consecutive peak heights agree within ± 3 percent of their average value. Check the spectrophotometer calibration frequently by running a blank and standard at least after every five samples; recalibrate as necessary.

It is also recommended that at least one sample from each stack test be checked by the Method of Standard Additions (See Citation 9, Section 11) to confirm that matrix effects have not interfered in the analysis.

9. Calculations

9.1 Abbreviations and Symbols

A_s = Stack area, m^2.

D.F. = Total dilution factor for the mercury containing solution before addition to the aeration cell.

$[Hg]_T$ = Total µg of mercury in the source sample after initial dilution.

$[Hg]_{s.c.}$ = Total ng of mercury in the aeration cell (from the calibration curve constructed as described in Section 8.4.2), corrected for solution blank value.

P_{bar} = Barometric pressure at the sampling site, mm Hg.

P_s = Absolute stack gas pressure, mm Hg.

R = Rate of mercury emission, g/day.

S = Aliquot size in ml added to the aeration cell.

T_m = Absolute stack temperature, °K.

v_s = Average stack gas velocity, m/sec.

V_m = Total volume of gas sample as measured by the dry gas meter, corrected for leakage, m^3.

V_{total} = Total gas sample volume (stack conditions), m3.

Y = Dry gas meter calibration factor.

ΔH = Average pressure differential across the orifice meter (see Figure 4), mm H_2O.

9.2 Calculate V_m, the total volume of dry gas metered (corrected for leakage, if necessary, as outlined in Section 6.3 of Method 5, Citation 1,2 in Section 11).

9.3 Calculate the volume of water vapor and the moisture content of the stack gas, according to Equations 5-2 and 5-3 of Method 5, (Citation 1,2, Section 11).

9.4 Calculate v_s, the average stack gas velocity, using Equation 2-9 of Method 2 (Citation 1,2, Section 11).

9.5 Calculate the total gas sample volume at stack conditions, using the following equation:

$$V_{total} = V_m Y \left(\frac{T_s}{T_m} \right) \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_s} \right) \qquad \text{Equation 1}$$

9.6 For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within ± 3 percent of their average for the contribution of the field blank.

Calculate the total mercury content, $[Hg]_T$, in each sample correcting for any dilutions made to bring the sample into the working range of the spectrophotometer.

9.7 Total Mercury Emission. Calculate the total amount of mercury emitted from each stack per day by Equation 2. This equation is applicable for continuous operations. For cyclic operations, use only the time per day each stack is in operation. The total mercury emissions from a source will be the summation of results from all stacks.

$$R = \left(\frac{(Hg)_T \qquad v_s \quad A_s}{V_{total}} \right) \left(\frac{86{,}400 \text{ seconds/day}}{10^6 \ \mu g/g} \right) \qquad \text{Equation 2}$$

9.8 Isokinetic Variation. Calculate percent isokinetic for each sampling run, as outlined in Section 6.11 of Method 5, 40 CFR 60, Appendix A.

10. Evaluation of Results

10.1 Acceptable Isokinetic Results.

10.1.1 The following range sets the limit on acceptable isokinetic sampling results:

If 90 percent ≤ I ≤ 110 percent, the results are acceptable. If the results are low in comparison to the emission standard and I is beyond the acceptable range, or, if I is less than 90 percent, the Administrator may opt to accept the results. Otherwise, reject the results and repeat the test.

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APPENDIX B
METHOD TO DETERMINE THE MERCURY CONTENT OF SEWAGE SLUDGE

1. Principle and Applicability

1.1 Time-composite sludge samples are withdrawn from the conveyor belt after dewatering and before incineration or drying. A weighed portion of the sludge is digested in aqua regia followed by oxidation by potassium permanganate. Mercury in the digested sample is subsequently measured by the conventional cold vapor technique.

1.2 Applicability. This method is applicable for the determination of total organic and inorganic mercury content in sewage sludges. The normal range of this method is 0.2 to 5 µg/g of sludge. This range may be extended above or below the normal range by increasing or decreasing sample size and through instrument and recorder control.

2. Apparatus

2.1 Sampling

2.1.1 Container, 50-liter, plastic

2.1.2 Scoop for removing sludge sample from conveyor line.

2.2 Mixing of Composite (8-hour) Sludge Sample

2.2.1 Mortar mixer, wheelbarrow-type, 57-liter (or equivalent) with electrically driven motor.

2.2.2 Blender, Waring-type, 2-liter.

2.2.3 Scoop for removing 100-ml and 20-ml samples of blended sludge.

2.3 Analysis

2.3.1 Atomic Absorption Spectrometer. Perkin-Elmer 303, or equivalent, containing a hollow cathode mercury lamp and capable of containing the optical cell described in Section 2.3.2.

2.3.2 Optical Cell. Cylindrical-shape with quartz end windows and having the dimensions shown in Figure 1. The cell is wire-wound with approximately 2 meters of 24 gauge nichrome heating wire and wrapped with asbestos insulation tape or equivalent; the wires must not touch each other.

2.3.3 Aeration Cell. Constructed according to the specifications in Figure 2. A glass frit is not an acceptable substitute for the blown glass bubbler tip shown in Figure 2.

2.3.4 Recorder. Matched to the output of the spectrometer described in Section 2.3.1.

2.3.5 Variac. To vary the voltage on the optical cell from 0 to 40 volts.

2.3.6 Hood. For venting optical cell exhaust.

2.3.7 Flow Metering Valve.

2.3.8 Flow Meter. Rotameter or equivalent, capable of measuring a gas flow of 1.5 liters/min.

2.3.9 Nitrogen Cylinder. Equipped with a single stage regulator.

2.3.10 Connecting Tubing. All connective tubing between the solution cell and the optical cell shall be made of glass (ungreased ball and socket connections are recommended). Tygon tubing, other types of flexible tubing, and metal tubing are unacceptable substitutes. Teflon, steel, or copper tubing should be used between the nitrogen tank and the flow meter valve (See Section 2.3.7). Tygon, gum, or rubber tubing may be used between the flow metering valve and the solution cell.

2.3.11 Flow Rate Calibration Equipment. Bubble flowmeter or wet test meter for measuring a gas flow rate of 1.5 liter/min. to within $\pm$ 0.1 liter/min.

2.3.12 Volumetric Flask. Class A with penny head standard taper stoppers; 100-ml.

2.3.13 Volumetric Pipets. Class A; 1, 2, 3, 4, and 5 ml.

2.3.14 Graduated Cylinder. 50 ml.

2.3.15 Magnetic Stirrer. General purpose laboratory type.

2.3.16 Magnetic Stirring Bar. Teflon coated.

2.3.17 Filter Paper. S & S No. 588 (or equivalent).

3. Reagents

3.1 Water. Distilled, meeting ASTM specifications for Type I Reagent Water-ASTM Test Method D-1193-72. At the option of the analyst, the $KMNO_4$ test for oxidizable organic matter may be eliminated when high concentrations of organic matter are not expected to be present. This water must be used in all dilutions and solution preparations.

3.2 Aqua Regia. Prepare immediately before use by carefully adding one volume of concentrated HNO_3 to three volumes of concentrated HCl.

3.3 Antifoam B Silicon Emulsion. J. T. Baker Co., (or equivalent).

3.4 Nitric Acid (15% V/V). Prepared by diluting 15 ml concentrated HNO_3 to 100 ml using distilled, deionized water.

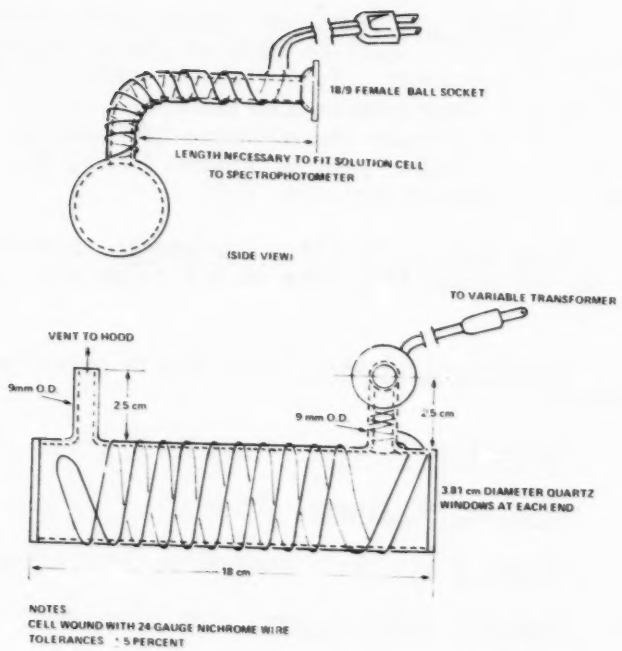

Figure 1. Optical cell.

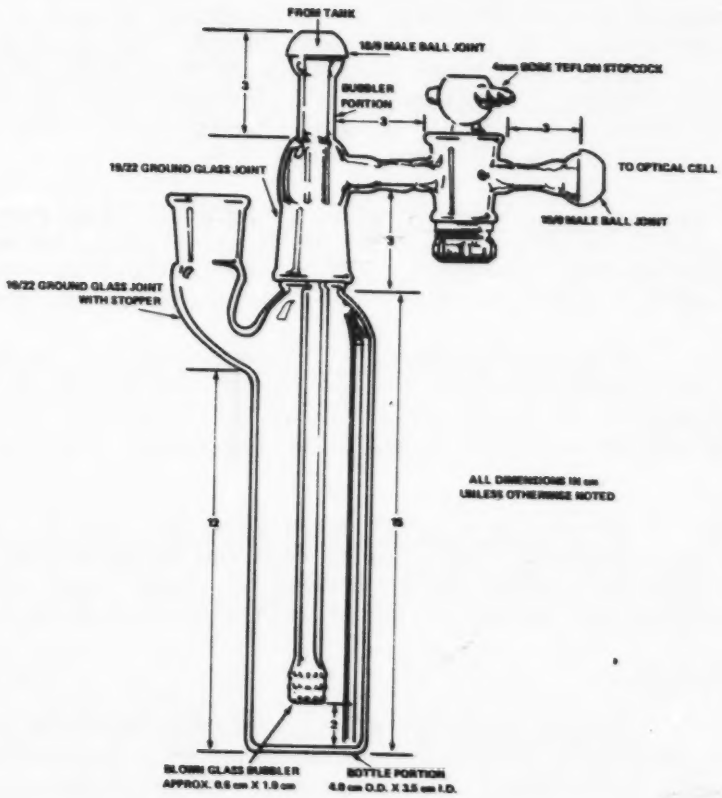

Figure 2. Aeration cell.

3.5 Sodium Chloride-Hydroxylamine Sulfate Solution. Dissolve 12 grams of sodium chloride and 12 grams of hydroxylamine sulfate in distilled water and dilute to 100 ml. Hydroxylamine hydrochloride may be used in place of the hydroxylamine sulfate.

3.6 Potassium Permanganate - 5% solution, w/v. Dissolve 5 grams of potassium permanganate in sufficient distilled water to make 100 ml.

3.7 Tin(II)Chloride Solution. Prepare fresh daily by dissolving 20 grams of tin(II)chloride in 25 ml concentrated HCl and dilute to 250 ml using distilled water. For an accurate and reproducible mercury analysis to be obtained, it is necessary to have a clear solution of tin(II)chloride. If the solution is cloudy, the tin(II) ion has been oxidized to tin(IV), and fresh reagent grade tin(II)chloride should be obtained. Alternately, a clear, tin(II)chloride solution is available from Perkin Elmer Corporation, Norwalk, Connecticut. Tin(II)sulfate may be substituted for the tin(II)chloride.

3.8 Mercury (II) Stock Solution (1 mg/ml). Completely dissolve 0.1354 g of ACS Reagent Grade $HgCl_2$ in 75 ml of distilled water, add 10 ml of concentrated HNO_3, and adjust the volume to 100.0 ml with distilled water. Mix thoroughly. (This solution should be stable for at least 1 month.)

3.9 Intermediate Mercury Standard Solution, 10 µg Hg/ml. Prepare fresh weekly. Pipet a 5.0 ml aliquot of the mercury stock solution into a 500-ml volumetric flask and add 10 ml of the 15 percent nitric acid solution. Adjust the volume to 500 ml using distilled water. Thoroughly mix the solution.

3.10 Working Mercury Standard Solution, 200 ng Hg/ml. Prepare fresh daily. Pipet a 5.0 ml aliquot from the "Intermediate Mercury Standard Solution" into a 250-ml volumetric flask. Add 5 ml of 1:1 nitric acid and adjust the volume to 250 ml with distilled water. Mix thoroughly.

4. Procedure

4.1 Sludge Sampling. Sludge samples should be withdrawn at a maximum of 30 minute intervals over an eight hour period and placed in a rigid plastic containers. A minimum of 25 kg of sludge should be obtained in this period.

4.2 Sludge Mixing. Transfer the entire 25 kg sample to a 57-liter capacity (2 ft^3) mortar mixer equipped with an electrically driven motor. (This operation is best done in a hood or outside). Allow the samples to mix for a minimum of 30 minutes at 30 rpm. Take six, 100-ml aliquots of sludge and combine in a 2-liter blender. Blend sludge for five minutes adding small portions of distilled deionized water as necessary to give a fluid consistency. Immediately after stopping the blender, use a small beaker to withdraw four, 20-ml aliquots of blended sludge and place them in separate, tared 125-ml Erlenmeyer flasks. Reweigh each flask to determine the amount of sludge added. (Three of the samples will be used to determine the mercury content in the sludge and the fourth will be used to measure the solids content of the blended sludge.)

4.3 Solids Content of Blended Sludge. Dry a 20-ml blended sample in an oven at 105°C until a constant weight is obtained. Allow to cool in a desiccator and record the dry weight of the sample.

4.4 Aqua Regia Digestion of Blended Samples. To each of the three remaining 20-ml samples from Section 4.2 add 25 ml of aqua regia and digest the samples on a hot plate at low heat for 30 minutes. Remove from the hot plate and allow to cool. (Samples should be a pale yellow-brown color and void of the dark brown color characteristic of organic matter.)

Filter each digested sample separately through S and S No. 588 filter paper and rinse the filter contents with 50 ml of distilled deionized water. Transfer the filtrate and filter washing to a 100-ml volumetric flask and carefully dilute to volume.

4.5 Solids Content of Sludge Before Blending. Remove two, 100-ml portions of mixed sludge from the mortar mixer and place in separate, tared 400-ml beakers. Dry in an oven at 105°C to a constant weight and cool in a desiccator.

4.6 Analysis for Mercury

4.6.1 Equipment Assembly. Assemble the aeration system as described in Figure 3.

4.6.2 Flow Calibration. Set the outlet pressure on the nitrogen cylinder regulator to a minimum pressure of 500 mm Hg (10 psi) and use the flow meter valve and a bubble flow meter or wet test meter to obtain a flow rate through the solution cell of 1.5 ± 0.1 liters/min. After flow calibration is complete, remove the bubble flow meter from the system.

4.6.3 Optical Cell Heating System Calibration. Using a 25-ml graduated cylinder, add 25 ml of distilled water to the bottle section of the aeration cell and attach it to the bubbler section. Attach the solution cell to the optical cell, and while aerating at 1.5 liters/min, determine the minimum Variac setting necessary to prevent condensation of moisture in the optical cell and in the connecting tubing. (This setting should not exceed 20 volts).

4.6.4 Spectrometer and Recorder Calibration. Set the spectrometer wavelength dial to 253.7 nm and make certain the optical cell is at the minimum temperature that will prevent water condensation from occurring. Then set the recorder to 90 percent of full scale as follows: Using a 25-ml graduated cylinder, add 25 ml of distilled water to the aeration cell bottle. Add three drops of Antifoam B to the bottle and then pipet a 5.0 ml aliquot of the working mercury standard solution into the aeration cell. (The mercury-containing solution should always be added to the aeration cell after the 25 ml of distilled water.) Place a Teflon-coated stirring bar in the bottle. Add 5 ml of 15 percent nitric acid and 5 ml of 5% potassium permanganate to the aeration bottle and mix well. Now, attach the bottle section to the bubbler section of the aeration cell, and make certain that: (1) the aeration cell exit arm stopcock (Figure 3) is closed (to avoid mercury prematurely entering the optical cell when the reducing agent is added); and (2) there is no flow through the bubbler.

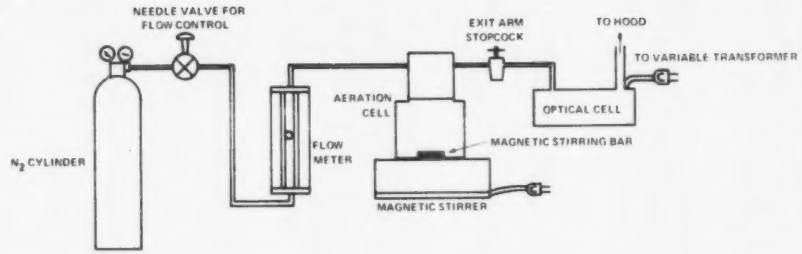

Figure 3. Schematic of the aeration system.

Add 5 ml of 12% sodium chloride hydroxylamine sulfate solution to the aeration bottle through the side arm and mix. If the solution remains un- clear, add additional sodium chloride hydroxylamine sulfate in 1-ml increments until the solution is colorless. Now add 5 ml of tin(II) chloride solution to the aeration bottle through the side arm and immediately stopper the sidearm. Stir the solution for 15 seconds, turn on the recorder, open the aeration cell exit arm stopcock and then immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard and set this value to read 90 percent of the recorder full scale.

4.6.5 Calibration Curve. Repeat the procedure in Section 4.6.4 using 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0-ml aliquots of the working standard solution. Repeat this procedure on each aliquot size until two consecutive peaks agree within 3 percent of their average value. The final amount of mercury in the aeration bottle for the 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml aliquots will be 0, 200, 400, 600, 800 and 1000 ng. Note: To prevent mercury carry-over from one sample to another, it is important that the nitrogen tank valve is open and that the aeration cell remains connected to the optical cell until the recorder pen has returned to the baseline and the sample is purged from the system. After separating the bottle and bubbler sections of the aeration bottle, place the bubbler section into a 600-ml beaker containing approximately 400 ml of distilled water and rinse the bottle section of the aeration cell with a stream of distilled water to remove all traces of the reducing agent. In order to prevent the loss of mercury prior to aeration, it is important to remove all traces of the reducing agent (tin(II)chloride) between samples. This is accomplished by washing with distilled water, however, washing the aeration cell parts with concentrated hydrochloric acid is necessary if any of the following conditions occur: (1) a white film appears on any inside surface of the solution cell; (2) a sudden change is observed in the calibration curve; (3) reproducible results are not obtained on replicate samples; or (4) following an abnormally high (in mercury content) sample.

Subtract the averaged peak height of the solution blank (0.0-ml aliquot) — which should be less than 2 percent of the recorder full scale — from the averaged peak heights of the 1.0-ml, 2.0-ml, 3.0-ml, 4.0-ml, and 5.0-ml aliquot standards. (If the blank absorbance is greater than 2 percent of full-scale, the probable cause is mercury contamination of a reagent or carry-over of mercury from a previous sample.) Plot the corrected peak height of each standard solution versus the corresponding final mercury concentration in the aeration cell (in ng) and draw the best fit straight line. This plot should either pass through the origin, or pass through a point no further from the origin than $\pm$ 2 percent of the recorder full scale. If a discrepancy occurs check for nonlinearity of the curve and for incorrectly prepared standards.

4.6.6 Analysis of Digested Samples. Repeat the procedure used to establish the calibration curve (Section 4.6.5) using an appropriate sized aliquot (1-10 ml) from the digested sample. (If the 10-ml sample is below the detectable limit, a larger aliquot should be used (up to 25-ml) but the volume of water added to the aeration cell should be decreased accordingly to prevent the solution volume from exceeding the capacity of the aeration bottle. If the peak maximum of a 1.0-ml aliquot of sample is off scale further dilution of the original sample must be

done to bring the mercury concentration into the calibration range of the spectrometer.

Analyze successive aliquots of each digested sample until two consecutive peak heights agree within ± 3 percent of their average value. Check the spectrometer calibration frequently by running a blank and standard at least after every five samples; recalibrate as necessary.

It is also recommended that at least one digested sample from each 8-hour composite sample be checked by the Method of Standard Additions to confirm that matrix effects have not interfered in the analysis.

5. Calculations

5.1 Nomenclature.

C_m = Concentration of mercury in the digested sample, µg/g.

F_{sb} = Weight fraction of solids in the blended sludge.

F_{sm} = Weight fraction of solids in the collected sludge after mixing.

M = Mercury content of the sewage sludge on a dry basis, µg/g.

m = Mass of mercury in the digested sample, µg.

V_a = Volume of digested sampled analyzed, ml.

V_s = Volume of digested sample, ml.

W_f = Weight of empty sample flask, g.

W_{fs} = Weight of sample flask and sample, g.

W_{fd} = Weight of sample flask and sample after drying, g.

Wb = Weight of empty sample beaker, g.

W_{bs} = Weight of sample beaker and sample, g.

W_{bd} = Weight of sample beaker and sample after drying, g.

5.2 Mercury Content of Digested Sample (Wet Basis). For each sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within ± 3 percent of their average for the contribution of the blank. Use the calibration curve and these corrected averages to determine the final mercury concentration in the solution cell for each sludge sample.

Calculate the total mercury content in each gram of digested sample correcting for any dilutions made to bring the sample into the working range of the spectrometer and for the weight of the sludge portion digested.

$$C_m = \frac{m\ V_s}{V_a\ (W_{fs} - W_f)} \qquad \text{Equation 1}$$

5.3 Solids Content of Blended Sludge. Determine the solids content of the 20-ml aliquot dried in the oven at 105°C (See Section 4.3).

$$F_{sb} = 1 - \frac{W_{fs} - W_{fd}}{W_{fs} - W_f} \qquad \text{Equation 2}$$

5.4 Solids Content of Bulk Sample (after mixing in mortar mixer). Determine the solids content of each 100-ml aliquot (See Section 4.5) as in Section 5.2 and average the results.

$$F_{sm} = 1 - \frac{W_{bs} - W_{bd}}{W_{bs} - W_b} \qquad \text{Equation 3}$$

5.5 Mercury Content of Bulk Sample (Dry Basis). Average the results from the three samples from each 8-hour composite sample and calculate the mercury concentration of the composite sample on a dry basis.

$$M = \frac{\bar{C}_m}{F_{sb}\ F_{sm}} \qquad \text{Equation 4}$$

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(Please read Instructions on the reverse before completing)

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15. SUPPLEMENTARY NOTES

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16. ABSTRACT

Two test methods for mercury are described along with the laboratory and field studies done in developing and validating them. One method describes how to homogenize and analyze large quantities of sewage sludge. The other test method describes how to measure the mercury emissions from the stacks of sewage sludge incinerators. In this latter method, the samples are collected in a potassium permanganate/sulfuric acid solution and analyzed for mercury using flameless atomic absorption.

17. KEY WORDS AND DOCUMENT ANALYSIS

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